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RESEARCH RELATED TO MEASUREMENTS OF ATOMIC SPECIES IN THE EARTH'S  
UPPER ATMOSPHERE

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## Introduction and Objective

Precise analysis by rocket- and satellite-borne mass spectrometers of the concentration of atomic oxygen in the earth's upper atmosphere is made difficult by the reactive character of the oxygen itself. This highly reactive species is able to interact with solid surfaces by adsorption, by formation of a solid oxide phase, and by catalytic production of molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from that of the environment due to atom removal on the various surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanism that are associated with the interaction of oxygen atoms with different solid surfaces under conditions similar to those encountered in the upper atmosphere.

The same difficulties in determining  $O/O_2$  ratios in the upper atmosphere are encountered when analyzing these entities in a laboratory experiment. To minimize such perturbations, the approach used in this study is to measure changes in oxygen atom concentration resulting from surface reaction and recombination in an environment where changes in both the oxygen pressure and the rate of production of oxygen atoms are negligible. The theoretical basis of the experimental approach was described in detail in the preceding Quarterly Status Report (September 1, 1967).

## Experiments

Initial experiments in the high-vacuum apparatus have demonstrated the general validity of the experimental approach for measuring the kinetics of interaction of gases at low pressures with metal surfaces. In addition, they have shown the relative magnitudes of the adjustable "sources" and "sinks" for gaseous species in the apparatus, such as the inlet and outlet conductances. Specifically, the sticking probability of molecular oxygen on platinum was measured.

In these experiments the specimen was a platinum foil with a geometric surface area of  $2.4 \text{ cm}^2$  situated in chamber C (Fig. 1). The foil was heated electrically to about  $1100^\circ\text{K}$  in a background pressure of  $5 \times 10^{-9}$  torr. Meanwhile, oxygen was admitted to chambers A and B through the servo-controlled leak valve, to maintain a steady-state pressure of  $5 \times 10^{-8}$  torr in chamber B. The ion gauge readings in A and B were continuously recorded. When shutter No. 2 was closed, followed immediately by the opening of shutter No. 1, the pressure in vessels B and C was equilibrated. The ion gauge recordings showed that approximately 10 seconds was required to restore the steady-state pressure in B and C to the value it had originally in B alone. The platinum specimen was thus rather suddenly exposed to a gaseous environment of fixed pressure. The rate of sorption of gas on this specimen was reflected in the change in gas flow into the system through the inlet conductance F.

Under the conditions described, the sorption rate, R, of the specimen is given by the change in the flow of gas through the inlet conductance. Hence:

$$R = F(P_A - P'_A) \quad (1)$$

where  $P'_A$  and  $P_A$  represent the pressures upstream of the conductance F before and after exposure of the specimen. Hence the recorded variation of  $P_A$  as a function of time gives a continuous indication of the gas sorption rate on the specimen. In addition, the total mass of gas adsorbed, M, as a function of time can be evaluated by integration:

$$M = F \int_0^t (P_A - P'_A) dt. \quad (2)$$

The removal rate of oxygen by surfaces in chamber C other than the specimen was examined in a separate experiment. After the platinum ribbon was covered with sorbed oxygen by exposure to  $\text{O}_2$  at  $P = 5 \times 10^{-8}$

torr for a prolonged period of time, chamber C was evacuated but the ribbon was not flashed. Subsequently, shutter No. 2 was closed and shutter No. 1 was opened. The pumping speed of chamber C was observed to be less than that observed with the flashed specimen by about a factor of four.

The results of these experiments are shown in Fig. 2 in which the variation of the sticking probability of oxygen on platinum is compared with the extent of surface coverage. Sticking probability,  $S$ , is the fraction of incident molecules which adsorb on the surface:

$$S = \frac{4 F (P_A - P'_A)}{\alpha P_{BC} v}$$

where  $\alpha$  is the area of the specimen,  $v$  is the mean molecular velocity, and  $P_{BC}$  is the pressure in vessels B and C.

A major problem encountered in our work is the generation of atomic oxygen. An initial experiment with a platinum filament for  $O_2$  dissociation demonstrated with increasing filament temperature an increase in mass 16 and a decrease in mass 32 on the quadrupole mass analyzer attached to chamber B. At  $1750^\circ K$ , the steady-state value of the ratio mass 32/mass 16 exceeded 0.3, but platinum vaporized at a rate sufficient to build up a visible deposit on the glass vessel wall adjacent to the ribbon within several minutes. This was considered to be a potential source of trouble. Hence, the platinum ribbon was replaced with a tungsten filament with a surface area of about  $4 \text{ cm}^2$ . Carbon impurity was leached from the filament by heating it to  $2300^\circ K$  in oxygen at  $P = 10^{-6}$  torr for about 8 hours. During this time the carbon monoxide observed in the system decreased markedly. However, even at filament temperatures exceeding  $2300^\circ K$  no significant enhancement in the oxygen atom concentration was observed. After this disappointing experiment, a new platinum ribbon was exchanged for the tungsten filament, but the earlier results could not be reproduced. Even at  $T > 1700^\circ K$ , the observed steady-state population of atomic oxygen, evidenced by the mass spectrometer, could not be enhanced.

## Discussion

The molecular oxygen sorption experiments on platinum are of some interest because they demonstrate that a significant fraction of the metallic surface is populated with sorbed oxygen rather quickly even at molecular oxygen pressures in the  $10^{-8}$  torr region. The data in Fig. 2 suggest that about 3 to 5% of the impinging molecules are sorbed until the surface coverage attains approximately one-tenth of a monolayer. If the oxygen is chemisorbed as atoms (which, from energetic considerations, is most likely the case), then gas-phase oxygen atoms would be expected to interact with this surface by a Rideal-Ely recombination mechanism. Such a reaction obeys first-order kinetics, and the rather extensive data on recombination kinetics obtained at higher pressures would be applicable. It is of interest to note that electrochemical studies of oxygen sorption on a platinum electrode have shown a maximum surface coverage of about 20%<sup>1</sup>. Also, the measured sticking coefficient is of the same magnitude, as that deduced from oxygen dissociation experiments<sup>2</sup> at  $T > 1700^\circ\text{K}$ .

Other means to generate atomic oxygen under the desired conditions of temperature and pressure are presently being considered. One potentially useful technique would be the photo-induced dissociation of ozone. Ozone is efficiently photo-dissociated into ground-state oxygen atoms  $[\text{O}(^3\text{P})]$  and oxygen molecules  $[\text{O}_2(^3\Sigma_g^-)]$  by light near 6000 Å with a high quantum yield. Such a technique should allow the dissociation reaction to be carried out in close proximity to the specimen, thereby reducing atom loss on other surfaces in the apparatus. A second technique being considered is the effusion of atomic oxygen from a heated furnace where it is generated at a pressure considerably higher than

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<sup>1</sup>M. L. B. Rao, A. Damjanovic, and J. O'M. Bockris, *J. Phys. Chem.* **67**, 2508 (1963)

<sup>2</sup>D. Brennan and P. C. Fletcher, *Trans. Farad. Soc.* **56**, 1662 (1960)

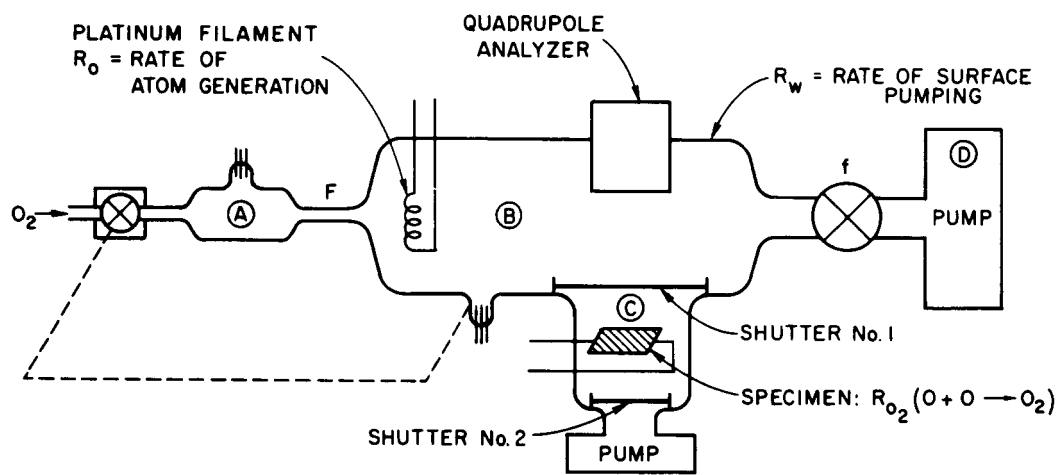
the working pressure in the apparatus. The rate of oxygen atom generation in a tungsten furnace at 2800°K has been shown to exhibit a first-order dependence on  $P_{O_2}$ , and at this temperature, oxygen atoms are the principal species obtained from the furnace<sup>3</sup>. Such a technique would require the addition of a pump to the apparatus to obtain an adequate differential pressure between the furnace and the specimen chamber.

#### Personnel

Staff members who have participated in this program during the past quarter include: Leon E. Hiam, Jan W. Van Gastel, Henry Wise, and Bernard J. Wood.

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<sup>3</sup>P. O. Schissel and O. C. Trulson, J. Chem. Phys. 43, 737 (1965)



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FIG. 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

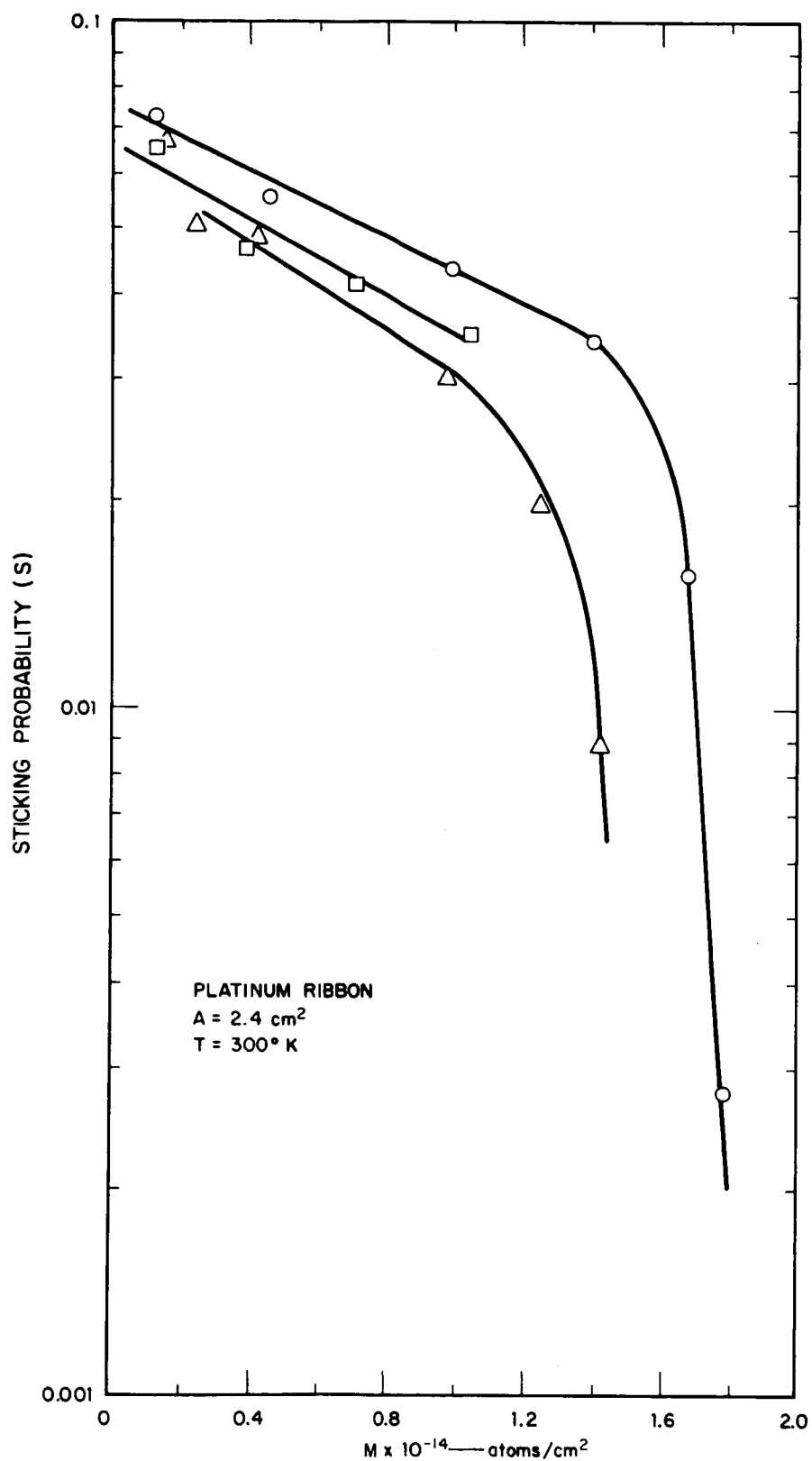


FIG. 2 STICKING PROBABILITY AS A FUNCTION OF ADSORBED OXYGEN